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Defect energy levels in HfO_2 high-dielectric-constant gate oxide

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This letter presents calculations of the energy levels of the oxygen vacancy and oxygen interstitial defects in HfO_2 using density functional methods that do not need an empirical band gap correction. The levels are aligned to those of the Si channel using the known band offsets. The oxygen vacancy gives an energy level nearer the HfO_2 conduction band and just above the Si gap, depending on its charge state. It is identified as the main electron trap in HfO_2. The oxygen interstitial gives levels just above the oxide valence band. © *2005 American Institute of Physics*.
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The continued scaling of complementary metal-oxide-semiconductor transistors requires the replacement of the SiO_2 gate dielectric by oxides of higher dielectric constant (κ) such as HfO_2 to avoid excessive gate leakage currents. However, HfO_2 suffers from a much higher defect density than SiO_2, which leads to large trapping in the insulator, lower carrier mobility in the transistor channel, threshold voltage shifts, and sources of instability.[1–6] Consequently, there is a need to identify the type of defects and their energy levels, in order to choose deposition and processing conditions to minimize the defect concentrations. Both oxygen vacancies and oxygen interstitials have been observed by electron spin resonance (ESR),[7,8] so it is unclear whether optimum conditions correspond to a high or low oxygen availability.

There have been a number of previous calculations[9–13] of the defect energies and energy levels in HfO_2. The oxygen vacancy and oxygen interstitial were identified as the two most likely intrinsic defects in terms of their formation energies.[9,10] The calculations also derived the energy levels. However, these calculations all used the local density approximation (LDA) of the local density formalism (LDF). The LDA is well known to give good total energies and structures, but to underestimate the bandgap of semiconductors and insulators by 30%–50%. For bulk materials, the underestimate could be corrected empirically by a rigid upward shift of the conduction bands to fit the experimental gap—the so-called "scissors operator." However, for defects, the energy levels are the heart of the problem. It is unclear in any empirical adjustment if a defect level should be moved in proportion to the gap or tied to a band edge. Indeed, the most complete study[9] places the O vacancy levels below the Si band gap in a $Si:HfO_2$ layer system, but experimental trapping data[5,6] require a level just above the Si gap. Thus, either the defect level is not a O vacancy or the calculated levels are wrong.

Ideally, an *ab initio* method should be used to find the defect energy levels. There are a number of methods, which can give improved band gaps, such as the GW approximation,[14] B3LYP,[15] self-interaction correction, and the screened exchange method.[16,17] The GW approximation was used to find the energy level of the ideal neutral O vacancy in ZrO_2,[14] but GW is a computationally quite expensive. Here we use two alternative methods to derive the energy levels, both within LDF; the screened exact exchange (sX) method and the weighted density approximation (WDA).[18] The sX method is based on Hartree-Fock, but introduces electron correlation via a simple screening term

$$V_{sX}(r,r') = -\sum_i \frac{\psi_i(r)e^{-k|r-r'|}\psi_j^*(r)}{|r-r'|},$$

where V_{sX} is the nonlocal screened exchange potential, ψ are the Kohn-Sham orbitals, and k is the Thomas-Fermi screening wave vector. In WDA, the exchange-correlation interaction is given by a Coulomb-like interaction between the electronic charge density n and the exchange-correlation hole of the electrons

$$\varepsilon_{xc}(r) = \int \frac{n(r)n_{xc}(r,r')}{|r-r'|}dr'.$$

ε_{xc} is the exchange-correlation energy density and n_{xc} is the exchange-correlation hole which is approximated by a particular functional form. These methods are found to give improved band gaps compared to LDA or generalized gradient approximation (GGA) methods. With the new methods, we find a sizable shift in the vacancy energy level, to a value more consistent with experiment.

The calculations use the total energy plane wave pseudopotential code CASTEP.[19] They use a supercell of 48 atoms of cubic or tetragonal HfO_2, containing a single vacancy or interstitial. The defect structures are relaxed in their various charge states using the PBE version of GGA. The vacancy energy levels are calculated with the sX method, using norm-conserving pseudopotentials and an energy cutoff of 600 eV. The interstitial levels are calculated in sX, and also in WDA and ultrasoft pseudopotentials and a cutoff of 450 eV.

The band gap of bulk HfO_2 is calculated to be 5.6, 5.95, and 5.75 eV in sX for cubic, tetragonal, and monoclinic phases respectively, and 6.1, 6.4, and 5.9 eV in WDA, compared to ~5.9 eV experimentally. This compares with LDA gaps of 3.7–4.3 eV.

Consider first the oxygen interstitial, denoted I. I^{2-}, the O^{2-} interstitial ion, is a closed shell system. It is well sepa-

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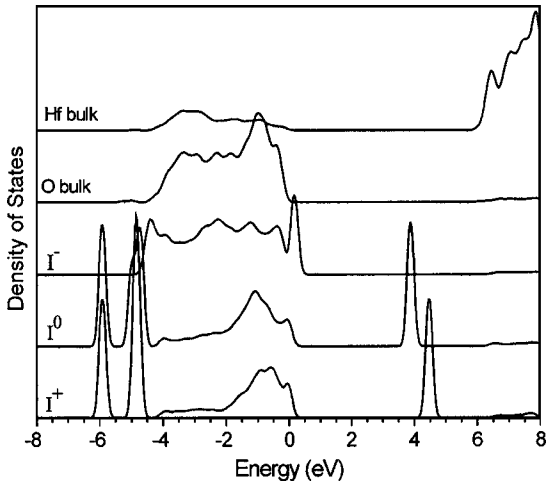

FIG. 1. Calculated local density of states at the relaxed oxygen interstitial in its various charge states.

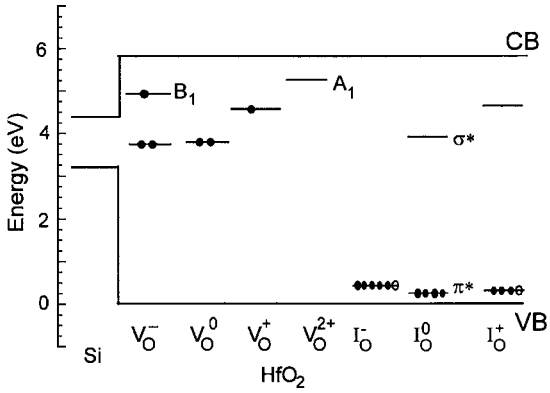

FIG. 2. Summary of calculated energy levels of the relaxed O vacancy and interstitial, in their various charge states.

rated spatially from other O^{2-} ions. Its local density of states (DOS) shows that its energy levels lie inside the oxide valence band. The I^- or O^- ion behaves similarly to O^{2-}. It lies about 2 Å from other O^{2-} ions. The local DOS of the O^- ion in Fig. 1 shows that it gives rise to a half-filled state about 0.5 eV above the valence band (VB) maximum. The I^0 or O^0 behaves differently. It has two holes and this causes it to form a O–O bond of length 1.49 Å to a bulk O^{2-} ion, and a dumbbell-shaped superoxyl ion O_2^{2-}. Its DOS has an empty antibonding σ^* state at 4 eV in the upper gap (Fig. 1). Its bonding partner lies at −6 eV in the valence band. There are also filled π and π^* states; the π^* state lies just above the VB edge.

The I^+ ion is also possible. This O^+ ion also forms a shorter O–O bond with a O^{2-} ion of 1.39 Å, giving a dumbbell O_2^- ion. It gives rise to an empty σ^* state in the upper gap at 4.5 eV, Fig. 1. It also has a filled π state and a half-filled π^* state. The Fermi level lies in the π^* state which lies just above the valence band top. This O_2^- ion is called the superoxyl radical. It is paramagnetic and its highly recognisable ESR signature was seen in HfO_2.[7]

Now consider the oxygen vacancy. The O vacancy creates a singly degenerate gap state of A_1 symmetry. It is occupied by two electrons for the neutral vacancy. The state is strongly localized on the *d* orbitals of the adjacent Hf ions. In *c*-HfO_2, the state of the relaxed neutral vacancy is calculated to lie at 3.8 eV above the oxide VB, Fig. 2. The ionic positions do not relax much from their ideal positions in the neutral vacancy, the Hf–Hf distance is 3.59 Å compared to 3.54 Å in bulk HfO_2.

At the positive vacancy, V^+, the A_1 defect state is now singly occupied. Its net positive charge causes the adjacent Hf^{4+} ions to relax outwards from the vacancy. The Hf–Hf spacing becomes 3.74 Å. This relaxation causes the defect state to move upwards from 3.2 to 4.7 eV, Fig 2. At V^{2+}, the A_1 state is now empty. The greater positive charge causes further outward relaxation of the Hf's so the Hf–Hf separation is now 3.90 Å. The gap state now lies higher at 5.2 eV due to the relaxation. A similar behavior is found for the vacancy in the other polytypes.

The vacancy can also trap one or two electrons. A trapped electron causes the adjacent Hf ions to distort asymmetrically, pulling down a singly degenerate B_1 state from the conduction band. This state can be occupied by one or two electrons. For V^-, it lies at 0.8 eV below the conduction band edge in sX (Fig. 2).

Figure 2 summarizes the levels of the vacancy and interstitial. The interstitial levels generally lie below midgap and the calculated energy levels of the vacancy lie in the upper gap. Using the valence band offset of HfO_2 on Si of ~3.3 eV,[20–22] we can position these energy levels against the Si bands. We find that the O vacancy levels lie above the Si conduction edge, particularly when charged. In contact with Si, the O vacancy will tend to be positively charged because it can transfer electrons into the Si, for example to acceptor states, even in the absence of any O interstitials.

The present vacancy level energies are much more consistent with experiment than the previous results. Takeuchi *et al.*[23] used spectroscopic ellipsometry on HfO_2 films oxidised to different levels to identify an absorption band at 4.5 eV. They attribute this to transitions from the HfO_2 valence band to the oxygen vacancy, and so place the V_O level at 4.5 eV in the gap. Brillson[24] observed cathodoluminescence at 3.7 and 4.5 eV which could be due to transitions from the valence band edge to these levels. Trapping data[3–6] indicates that HfO_2 possesses bulk electron traps lying below the oxide conduction band (CB). Kerber *et al.*[3] noted that this trap must lie just above the Si conduction edge. Mitard[25] positions trapping levels at ~2.1 eV and 0.8 eV below the oxide CB, that is, at ~0 and 1.3 eV above the Si midgap energy. Kumar's[4] data are not consistent with a level lying below the Si valence band edge. Again, this is consistent with our levels, assuming some valence band tailing. Note that the electron trap must correspond to V^-, not V^+, as assumed by others.[11,12]

The previous calculations of the oxygen V^0 levels in ZrO_2 and HfO_2 by Foster[9,10] placed the levels at 2.1 and 2.9 eV above the oxide VB edge. This low value is fundamentally because of their LDA correction method, which tied the vacancy levels to the VB as the gap was opened up from 3.5 to 5.5 eV. This resulted in vacancy levels lying below the Si VB edge. A proportional shift of the vacancy levels upwards would have given results closer to ours. The GW result of Kralik[14] place the vacancy levels higher, at ~3.4 eV above the oxide VB, and perhaps a little higher if the gap is increased to the experimental value. Our results place the V^+ level in HfO_2 much higher than Foster,[9,10] and above the Si CB edge. Other LDA-only calculations by, for example, Shen *et al.*[12] found higher vacancy levels, because they did

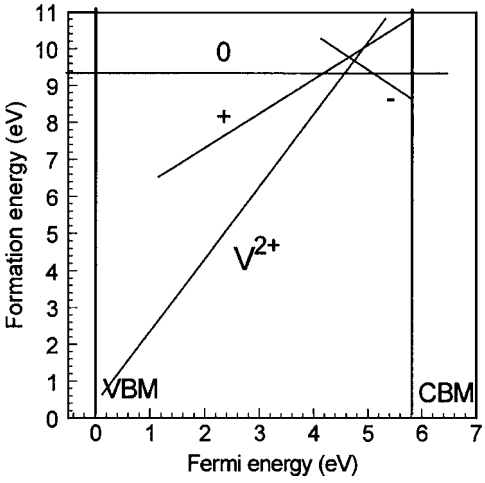

FIG. 3. Formation energy of the O vacancy with respect to atomic O vs Fermi level position.

not apply any correction. However, these results are unreliable because some correction is needed.

The consistency of our results with trapping data implies that the O vacancy is the dominant defect in HfO_2 gate oxide films. It means that conduction in HfO_2 films is by electrons, by Poole-Frenkel hopping or trap assisted tunneling.[26] The trap depth is therefore of order 1–1.5 eV, that of V^+ below the oxide conduction band edge.

Gusev *et al.*[27] recently found that the charge trapping in HfO_2 depends on the nature of the gate electrode. Conventional polycrystalline (poly)-Si gates caused strong trapping, while W gates gave much less trapping. The poly-Si is formed under reducing conditions after the HfO_2. This further suggests that O vacancies are the source of traps and could be related to O out-diffusion in HfO_2. Hf silicates are less prone to this problem. Hole transport would occur through states associated with any O interstitials.

The vacancy level in HfO_2 compares to the O vacancy level in MgO where it lies at about midgap. This is consistent with the lower ionicity of HfO_2 than MgO. The sensitivity of the O vacancy level in HfO_2 to its relaxation occurs because its state is localized on the adjacent metal orbitals, as also seen in Refs. 14 and 10. In contrast, in MgO the state is localized *inside* the vacancy itself.

We have also derived a formation energy diagram for the O vacancy (Fig. 3). The formation energy of V^0 is taken from Foster,[9] and that of the charged states from our calculated energy levels. We see that V^+ possesses a negative correlation energy or "*U*." The single positive state V^+ is unstable with respect to V^0 and V^{2+}. This was also proposed by Shen[12,28] but on the basis of LDA calculations with a band gap error. However, their analysis applied to hole traps, rather than the electron traps of interest.

In conclusion, we find that the oxygen vacancy gives levels near or above the Si conduction band edge, indicating it is the main charge trap in HfO_2:Si layers. As the principle trap in HfO_2, this suggests that deposition and postprocessing conditions should aim to remove or passivate these defects, with an oxygen-rich ambient.

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